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The effect of microwave pretreatment on biogas production from agricultural straws

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HIGHLIGHTS

- ▶ Barley, spring wheat, winter wheat and oat straw were examined.
- ▶ Microwave pretreatment were performed at 200 and 300 °C.
- ▶ The biogas production performance was investigated.
- ▶ Specific methane yields were not improved by microwave irradiation.
- ▶ Conversion yield and cumulative biogas production have inverse relations.

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ABSTRACT

Biogas production from microwave-pretreated agricultural residual straws that are used as feedstock was investigated in a laboratory batch study. Barley, spring wheat, winter wheat and oat straw were examined. To investigate the effect of changing the physicochemical structure of the straws on biogas production, the pretreatment processes were applied to two sample groups. The first group contained milled straw and the second group comprised milled wet straw that was prepared by the addition of deionized water. Both groups were subjected to microwave irradiation until oven temperatures of 200 or 300 °C were attained. Sixty-six identical batch anaerobic reactors were run under mesophilic conditions for 60 days. Preliminary test results showed that the microwave pretreatment of the different straws did not improve their anaerobic digestion. An increase in the treatment temperature led to lower biogas production levels. An inverse relationship between the thermal conversion yield and cumulative biogas production was observed.

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1. Introduction

Studies on the conversion of whole crop cereals and their residues into energy and valuable chemicals show very promising future applications. In recent years, the anaerobic digestion process has been used to obtain energy from lignocellulosic residues in co-digestion, because it provides a higher content of carbon for the digestion. The different types of lignocellulosic biomass vary in the percentages of the major constituents, i.e., cellulose, hemicelluloses, lignin, organic extractives and inorganic minerals, depending on their origin and species (Mohan et al., 2006). The cellulose chains are packed by hydrogen bonding in “elementary microfibrils.” These fibrils are attached to each other by hemicelluloses and by other polymers such as pectin and are covered by lignin. The microfibrils often associate as bundles or macrofibrils. These strong chains form a crystalline ribbon that makes cellulose resistant to biological treatments by making it less available for microbial and enzymatic hydrolysis. Consequently, the most rate-limiting stage of biomass degradation is reported to be the hydrolysis stage of the digestion process. Similarly, lignocellulosic biomass must be pretreated to make it less resistant and more exposed for improved hydrolysis efficiency (Zhu et al., 2010). Pretreatment is a process that makes biomass more hydrolysable than it is in its hydrolysis-resistant native state. There are many pretreatments technologies, such as thermal, biochemical, mechanical and enzymatic treatments (Estevez et al., 2012; Jackowiak et al., 2011). To observe the pretreatment effects, anaerobic batch experiments are employed to determine the biochemical methane potential of the pretreated biomass (Jackowiak et al., 2011; Zhu et al., 2010).

In thermal pretreatment, heat is either transferred into the material through convection, conduction or radiation using conventional heating, or it is delivered directly into the material through molecular interaction with an electromagnetic field using microwave energy. The electromagnetic energy of the microwave radiation is converted to thermal energy. The microwave technique has many potential advantages, as it penetrates materials, deposits energy and generates heat throughout the volume of the material.

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The transfer of energy enables the achievement of rapid and uniform heating of materials. The use of microwave energy reduces the heating period of the material (Thostenson and Chou, 1999). The potential advantages include not only uniform heating of the material and reduced processing time but also increased energy efficiency, rapid and controlled heating and exceptional control over the heating process (Nour et al., 2010; Robinson et al., 2010; Huang et al., 2008).

The microwave irradiation could lead to one or more changes in the features of the cellulosic biomass, including increased specific surface area, decreased polymerization and crystallinity of the cellulose, hydrolysis of the solubilized oligomers of hemicellulose and partial depolymerization of lignin (Odhner et al., 2012). It can make the substrate more accessible to enzymes due to increased availability of contact surfaces and decreased crystalline structure. Therefore, thermal pretreatment using microwave radiation may be a good method for biomass pretreatment, as it disrupts the complex and rigid structure of the biomass that makes it resistant to mechanical stress and enzymatic attack. Although the irradiation has been widely applied to pyrolysis processes as an established and promising method for producing syngas, pyroloictic liquids (tar and pyroligneous acids) and chars (Robinson et al., 2010), only a few of studies have been devoted specifically to the study of microwave irradiation (under atmospheric condition) for the pretreatment of biomass (Jackowiak et al., 2011). Thermal pretreatment by microwave irradiation may be a good candidate for the pretreatment of biomass because it disrupts the complex lignocellulosic structure. Hence, the applicability of microwave irradiation needs to be evaluated for the pretreatment of lignocellulosic material.

A study emphasized that during the microwave irradiation of biomass, the moisture is removed as the temperature rose from ambient temperature to 100 °C (De Wild et al., 2011). Degradation of the biomass to decompose its components by slow pyrolysis has demonstrated that hemicellulose is lost at temperatures ranging from 130 to 194 °C (Mohan et al., 2006). Another pyrolysis study showed that hemicelluloses, cellulose and lignin collapse at temperatures ranging from 197 to 257 °C, 237 to 347 °C and 277 to 497 °C, respectively (Demirbas, 2004). Large amounts of hemicelluloses and cellulose are destroyed when biomass is torrefied at 290 °C (Medic et al., 2012; Chen and Kuo, 2011).

The objective of this study was to determine the effects of microwave pretreatment on the digestibility of Norwegian agricultural residual materials under anaerobic mesophilic conditions. Four different types of agricultural straws, winter wheat (WW), spring wheat (SW), oat straw (OS) and barley straw (B), were selected and the biogas potential was investigated. Two wheat straws, WW and SW, were investigated separately because of their different characteristics. SW has no vernalization requirement and develops reproductively in response to increasing temperature and photoperiod, while WW development is based on a vernalization requirement rather than the season when they are usually sown (Loomis and Connor, 1998).

2. Methods

2.1. Biomass collection

WW, SW, OS and B were collected from locations near the around the Norwegian Agricultural University of Life Sciences campus in Aas, Norway. After the harvest period (fall of 2010), all of the straw materials were baled in a plastic bag in the field. Thermal conversion requires the feedstock to be dried, which is an energy-intensive process (Wang et al., 2008). This process is energy intensive because the bales were not opened until their arrival at the laboratory where the experimental equipment was available.

2.2. Drying and milling processes

Before starting the experiments, the materials were stored at room temperature to minimize temperature differences and to remove the undesired moisture content. To obtain small particle sizes of the straws, the air-dried straws were milled (2000 rpm, 3 min) using a Retsch Knife Mill (GRINDOMIX GM 300 – Germany) and were then referred to as milled straw (MS). Each type of MS was manually mixed in a large plastic container for approximately 10 min to obtain a uniform environment in the feeding material. The homogenized MS was then stored at room temperature until further use.

The particle size distributions of the four types of milled straws are given in Fig. 1. Table 1 indicates the results of their proximate and physico-chemical properties.

2.3. Microwave pretreatment process

A microwave experiment was conducted in a laboratory-scale CEM Microwave Max asphalt oven (15 Amps, 50 Hz for 220–240 V). The oven's original thermocouple sensor was positioned inside the microwave after it was calibrated using another sensor (TENMA 72-7712 CE dual-input digital thermometer, type K thermocouple probes); thereafter, the temperature nearby the reactor was adapted to express the relative thermal effect of microwave power in accordance with the work of Huang et al. (2008). The average heating rate was 5 °C min^{-1}. Microwave pretreatment of MS (100 g) was performed at 200 and 300 °C with a hold time of 15 min. The procedures were not run in the complete absence of air, which distinguishes them from the procedure used for torrefaction (mild-pyrolysis) (Medic et al., 2012). After the microwave pretreatment process, the solid residues were allowed to cool to approximately 100 °C and placed in desiccators for around 3 h. The solid residues were weighed at room temperature (Huang et al., 2008). The final weight of the sample was determined to calculate the solid yield (SY) (%) according to the pyrolysis process, even though the process used differed from pyrolysis because it was performed in the presence of air. To determine the amount of organic matter (OM) (g), Eq. (1) was used and the SY was calculated according to Eq. (2). Depending on the SY, the pyrolysis conversion (PC) ratio was obtained using Eq. (3):

$$\mathrm{OM(g)} = \mathrm{AM(g)} - [(\mathrm{PA}(\%) + \mathrm{PM}(\%))/100] \cdot \mathrm{AM(g)} \tag{1}$$

$$\mathrm{SY}(\%) = [[\mathrm{CP(g)} - (\mathrm{AM(g)} \cdot \mathrm{PA}(\%)/100)]/[\mathrm{AM(g)} - (\mathrm{AM(g)} \cdot \mathrm{PA}(\%)/100)]] \cdot 100 \tag{2}$$

$$\mathrm{PC}(\%) = 100 - \mathrm{SY}(\%) \tag{3}$$

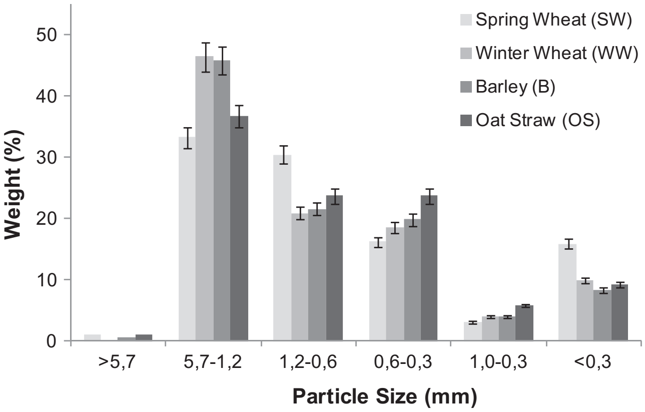

Fig. 1. Particle size distribution of the milled straws (MSs).

Table 1
Proprieties of the milled straws (MS).

Constituent		B	SW	WW	OS
Proximate analysis (wt.%[a] ± MU[b])	Moisture	6.11 ± 10	6.0 ± 10	5.9 ± 10	6.8 ± 10
	Volatile matter	74.7 ± 5	74.1 ± 5	74.9 ± 5	70.6 ± 5
	Ash	4.1 ± 10	3.3 ± 10	4.0 ± 10	7.0 ± 10
	Fixed Carbon	15 ± 7	16.5 ± 7	15.2 ± 7	15.7 ± 7
Cellulose (ADF-ADL) (g/100 g)		45	46.4	44.0	43.8
Hemicelluloses (NDF–ADF) (g/100 g)		24.2	26.4	30.0	23.2
Lignin (ADL)(g/100 g)		9.0	8.6	8.0	8.2
Calorific value (MJ/dw[c] kg ± MU[b])		18.8 ± 5	19.2 ± 5	19.0 ± 5	18.3 ± 5
Ultimate analysis (TM%[d] ± MU[b])	C	47.7 ± 5	48.4 ± 5	47.9 ± 5	46.4 ± 5
	H	5.6 ± 10	5.7 ± 10	5.8 ± 10	5.4 ± 10
	N	0.4 ± 10	0.6 ± 10	0.5 ± 10	0.4 ± 10
	O	41.5	41.6	41.6	39.4
Physicochemical analysis	pH	7.6 ± 0.2	7.4 ± 0.0	7.59 ± 0.0	8.2 ± 0.0
	Conductivity (μS/cm)	903.0 ± 1.4	982.5 ± 3.54	428.5 ± 0.7	1433 ± 17
	Salinity	0.40 ± 0.0	0.5 ± 0.0	0.2 ± 0.1	0.80 ± 0.0
	Total dissolved solid (mg/l ± SD[e])	1002.5 ± 0.7	1110 ± 2.8	486.5 ± 2.1	1601.5 ± 13.4

[a] Weight presence of mass.
[b] Measurement uncertainty (%).
[c] Dry weight.
[d] Total matter.
[e] Standard deviation ($n = 3$).

where AM is the amount of matter in the raw material (MS), PA is the percentage of ash in MS, PM is the percentage of moisture in MS and CP is the char product (pretreated straw) (modified from Şimşek, 2006).

Microwave pretreatment experiments on the four different types of MS were conducted in two groups. The first group was operated with MS (100 g) that was dried at room temperature before the microwave treatment, and the second group was run with wet MSs that were prepared by the addition of deionized water at a weight equal to that of the straw weight in the microwave reactor (w:w) to investigate the pretreatment effects of the cracked straw structure on the biogas methane potential. The wet feedstocks were named “+W”.

2.4. Anaerobic digestion process

Sixty-six identical, 1125 ml laboratory-scale anaerobic batch reactors were run in triplicate to investigate the methane yield of pretreated straws at the same organic load, retention time and incubation conditions.

In this study, an inoculum composed of cattle manure and food waste that originated from the biogas plant at Tomb’s Agricultural College in Norway was used. The inoculum was preincubated under anaerobic conditions at 37 ± 0.5 °C for 2 weeks prior to inoculation. After 2 weeks, when the batch reactors were fed by substrate (or cellulose for the control reactor) as quickly as possible, the lip of the blank reactor was open for about the same amount of time to create a similar condition. The pH, conductivity (μS/cm) and salinity values of the inoculum were found to be 7.44 ± 0.1, 23.4 ± 0.1 and 16.05 ± 0.07, respectively. Following preincubation, the vials were filled with diluted inoculum (700 ml, approximately 6 g VS/l) and each of the pretreated straw substrates (approximately 4 g VS/l) according to recommended substrate-inoculum ratios in the literature (Angelidaki et al., 2009, Raposo et al., 2006).While filling the vials, the inoculum tank was continuously stirred with a magnetic rod to prevent the sedimentation of suspended particles. After the addition of the substrates, the vials were closed with rubber stoppers and aluminum crimps. In addition, the diluted inoculum (without the substrates) was run as a blank and with pure cellulose ($(C_6H_{10}O_5)n$, <20 μm Merck Chemical Corp.) as a control. Finally, the vials were incubated (90 rpm, 37 ± 0.5 °C) and biogas production was observed by measuring the developed pressure. Excess pressure was released via needle insertion into the rubber stoppers.

2.5. Analytical methods

To determine the particle size of the MS, the samples were screened with the Endecotts test sieves mesh series (England). Values for pH, conductivity, total dissolved solids (TDS) and salinity of all MS were determined using a WTW Multi 350i after the MSs were diluted with ultra pure-water (1:5), using the protocol described for solid analyses by Blakemore et al. (1987). Analyses of the ultimate, proximate and calorific values and the carbohydrate content of the straw samples were performed by a commercial laboratory (Eurofins Norsk Miljøanalyse AS in Norway). The proximate, calorific values and neutral detergent fiber (NDF) were determined using standard methods of the European Committee for Standardization (CEN) (Table 1). Acid detergent lignin (ADL) and acid detergent fiber (ADF) were determined using the standard method of Association of Official Analytical Chemists (AOAC, 2006). The amount of hemicelluloses in each sample was calculated by NDF–ADF. Elemental analysis was performed by both the CEN and the American Society for Testing and Materials standards (ASTM, 2008).

The biogas volume of each anaerobic batch reactor was determined by measuring the amount of pressure (GMH 3161 Greisinger Electronic, Germany) in the vials (Eskicioglu et al., 2009). The volume of the headspace was calculated using the following equation (Eq. (4)) as described by Estevez et al. (2012), based on the European Chemical Industry Ecology and Toxicology Center (ECETOC) procedure

$$V_{\text{biogas}} = (n.R.273)/P_0 = [(dP.V)/(R.T)].[(R.273)/P_0] = (dP.V.273)/(T.P_0) \quad (4)$$

where V_{biogas} is the volume of biogas (l) at standard conditions (0 °C and 1 atm); P_0 is 1 atm; V is the headspace volume (l); T is the incubation temperature (K); R is the ideal gas constant (0.08205 atm l/mol K); and dP is the pressure difference between the initial and final readings (atm).The methane yield was determined by measuring the methane concentration in the headspace using an SRI gas chromatography instrument (Model 8610 C)

Table 2
Chemical and textural characteristic of pretreated straw (wt.%).

Experimental name	Average temp (°C)	SY (% ± SD[a])	PC (%)	Moisture (% ± SD[a])	Cellulose (g/100 g)	Hemi-cellulose (g/100 g)	Lignin (g/100 g)	C (%)	H (%)	C/N	pH (value ± SD[a])	Conductivity (μS/cm ± SD[a])	Salinity (value ± SD[a])	TDS (mg/l ± SD[a])
B 200 °C	200	86.4 ± 9.6	13.6	1.71 ± 0.14	45	20	14.0	49.2	5.5	102.5	6.2 ± 0.1	895.5 ± 14.9	0.4 ± 0.0	1005.5 ± 0.7
B 300 °C	300	41.1 ± 0.8	58.9	1.22 ± 0.01	19	1.4	63.0	65.9	4.0	92.8	8.3 ± 0.1	1065.5 ± 2.1	0.5 ± 0.0	1190.5 ± 3.5
B + W 200 °C	200	50 ± 10.5	50	2.45 ± 0.31	46.8	19.9	12.2	48.4	5.6	110	6.2 ± 0.1	568.0 ± 0.1	0.2 ± 0.0	656.5 ± 2.1
B + W 300 °C	300	21.7 ± 0.4	78.3	1.04 ± 0.12	23.5	<DL[b]	58.5	64.0	4.1	92.8	8.0 ± 0.1	962.5 ± 0.7	0.4 ± 0.0	1056 ± 42.4
SW 200 °C	200	78.4 ± 2.2	21.6	1.38 ± 0.08	46.9	16.6	19.1	52.9	5.5	91.2	6.0 ± 0.1	474.0 ± 1.4	0.3 ± 0.0	682.0 ± 2.8
SW 300 °C	300	4.3 ± 1.1	58.7	1.15 ± 0.16	19.4	0.6	65.6	67.3	4.2	83.1	8.1 ± 0.1	629.5 ± 0.7	0.2 ± 0.0	528.5 ± 0.7
SW + W 200 °C	200	37.6 ± 10.6	62.4	1.50 ± 0.16	43.3	20.3	19.7	53.1	5.5	88.5	6.8 ± 0.1	497.5 ± 3.5	0.2 ± 0.0	564.5 ± 0.7
SW + W 300 °C	300	24.1 ± 1.2	75.9	1.12 ± 0.02	30.4	0.7	54.6	63.9	4.7	83	7.9 ± 0.2	751.0 ± 12.7	0.4 ± 0.1	856.0 ± 5.7
WW 200 °C	200	90.9 ± 6.6	9.1	1.51 ± 0.02	45.8	24	11.2	48.8	5.6	92	5.8 ± 0.1	396.0 ± 1.4	0.1 ± 0.0	438.0 ± 9.9
WW 300 °C	300	44.3 ± 2.3	55.7	0.87 ± 0.06	21.6	<DL[b]	62.4	65.5	4.3	78.9	8.0 ± 0.1	620.5 ± 2.1	0.3 ± 0.0	694.0 ± 1.4
WW + W 200 °C	200	48.1 ± 2.1	51.9	2.82 ± 0.04	46.9	20.9	12.1	51.3	4.7	96.8	5.8 ± 0.1	495.0 ± 2.8	0.2 ± 0.0	539.0 ± 5.7
WW + W 300 °C	300	24.7 ± 1.2	75.3	0.0 ± 0.13	39.8	1.9	40.2	60.0	4.3	81.1	7.5 ± 0.1	343.5 ± 0.7	0.1 ± 0.0	378.5 ± 2.1
OS 200 °C	200	78.4 ± 4.8	25.2	0.31 ± 0.02	46.8	11.3	15.2	51.5	5.3	114.4	7.5 ± 0.1	1710 ± 7.1	0.9 ± 0.0	1910.5 ± 0.7
OS 300 °C	300	31.3 ± 0.9	68.7	1.60 ± 0.27	14.9	<DL[b]	59.1	60.8	1.2	164.3	9.4 ± 0.1	4735 ± 7.1	2.6 ± 0.2	4255 ± 7.1
OS + W 200 °C	200	44.7 ± 2.5	55.3	1.25 ± 0.0	45.9	19.4	10.1	48.2	5.4	123.6	7.9 ± 0.1	1960 ± 2.8	1.3 ± 0.1	1751.5 ± 33.2
OS + W 300 °C	300	18.6 ± 3.9	81.4	0.05 ± 0.19	21.4	<DL[b]	52.6	71.3	2.5	115	8.8 ± 0.1	1662 ± 11.3	1.3 ± 0.1	1704.5 ± 3.5

[a] Standard deviation ($n = 3$).
[b] Detection limit.

equipped with a thermal conductivity detector (TCD) and a 3′ × 1/8″ s.s. molecular sieve, 13× stainless steel column. The operational temperatures of the injector, detector and column were kept at 41, 153 and 81 °C, respectively. Helium was used as a carrier gas at a flow rate of 20 ml/min. A gas mixture of CH_4/CO_2 (65/35%) was used as the standard gas mixture for calibration. The gas chromatogram was analyzed using the PeakSimple 3.67 program.

The reported methane yields were calculated as the difference between the methane produced by the vials with substrates and that produced by the blank vials (without substrate).

2.6. Statistical analysis

Particle size discriminations of each straw were evaluated using a one-way ANOVA performed using the Minitab®16 statistical software package. An alpha (α) level of 0.05 was used to determine the statistical significance of all analyses. The results were expressed using the mean, standard deviation and individual 95% confidence interval of the mean to reflect the statistically significant difference between the groups. To calculate the SY and the PC of the thermal pretreatment, the microwave pretreatment experiments were carried out in triplicate. The biogas volume and the biogas quality in the anaerobic batch systems were performed in triplicate. The properties of all initial straws and inoculum and the final liquid (digestate) quality of the anaerobic batch systems were determined in duplicate. Experimental results were reported as the average value of each parameter with a standard deviation. All standard deviations reported in this study were calculated using the statistical functions in Microsoft Excel® 2007. To explore the influence of thermal pretreatment, biogas production and the composition of the biogas produced by the different types of MS were compared using a paired t-test with the Minitab® 16 statistical software package.

3. Results and discussion

3.1. Milling straws

It has been reported that the particle size of a sample influences its compositional analysis. Biomass samples with larger particle sizes displayed higher cellulose, hemicellulose and lignin levels and a lower ash level than the fractions with smaller particle sizes (Ross and Mazza, 2011). Therefore, before the effect of particle size was controlled in this work, the content of the carbohydrate components was analyzed to understand the changing carbohydrate composition in the microwave-pretreated straws and the contents of cellulose and hemicellulose of the untreated straw types (B, SW, WW and OS) were measured.

To determine the effect of particle size on the pretreated MS, particle size variations of untreated MS were investigated. No significant differences were observed between the means of the four straw types ($p > 0.05$) (Fig. 1). The contents of the cellulose and hemicelluloses in MSs were found to be similar to those reported in the literature (Ross and Mazza, 2011; Deniz et al., 2004), but the lignin contents of MSs were found to be lower than but similar to the results observed by Jackowiak et al. (2011) and Antongiovanni and Sargentini (1991). In regards to the properties of the four types of MS, WW had the highest concentration of hemicelluloses and the lowest TDS concentration, salinity and conductivity compared to the other investigated straws (Table 1). The highest amounts of fixed carbon and cellulose were detected in SW. Changes in the levels of the carbohydrate and nitrogen fractions in the wheat during their growth in cold and warm environments have been observed by Murray (2004). It was reported that the temperature during germination of wheat seeds or seedlings is significant. For example, exposure to cold temperatures must be continuous and not interrupted by warm temperatures during the WW vernalization process (Murray, 2004) because temperatures above 10 °C can stop or reverse the process. The different properties of the investigated wheat straws (SW and WW) were most likely due to vernalization requirement differences and large species-based variations, as reported by Antongiovanni and Sargentini (1991).

3.2. Physical characteristics and chemical composition of the pretreated straws

Batch experimental results showed that microwave-pretreated MSs were darker in color than the samples from untreated MS. Upon further increase of the temperature from 200 to 300 °C, the colors of each pretreated straw ranged from light brown to dark brown (almost black). Lanzetta and Di Blasi (1998) observed similar phenomena for the color change of wheat straws and corn stalks at 375 °C with rapid heating. Furthermore, the present study

Table 3
Cumulative biogas production and cumulative methane production of untreated as control and pretreated straws after 60 days trial time.

Experimental name	Cumulative biogas production (ml biogas. gVS^{-1})	Cumulative methane production (ml CH_4. gVS^{-1})
B	406.0 ± 13.9	226.4 ± 8.5
B 200 °C	425.1 ± 4.8	223.4 ± 2.2
B 300 °C	25.2 ± 23.6	23.5 ± 15.4
B + W 200 °C	265.6 ± 33.1	149.6 ± 20.0
B + W 300 °C	18.9 ± 12.5	15.5 ± 8.4
SW	434.18 ± 19.5	234.0 ± 10.3
SW 200 °C	153.4 ± 28.3	83.0 ± 16.4
SW 300 °C	20.6 ± 18.5	18.6 ± 12.0
SW + W 200 °C	119.0 ± 34.4	72.2 ± 20.9
SW + W 300 °C	55.8 ± 12.4	37.0 ± 8.2
WW	540.4 ± 34.6	277.8 ± 19.1
WW 200 °C	174.0 ± 4.2	98.0 ± 2.2
WW 300 °C	25.7 ± 18.3	21.5 ± 11.8
WW + W 200 °C	320.4 ± 16.7	167.0 ± 8.0
WW + W 300 °C	77.8 ± 30.8	51.5 ± 19.8
OS	481.3 ± 42.6	246.4 ± 21.4
OS 200 °C	177.7 ± 17.3	106.8 ± 10.5
OS 300 °C	1.8 ± 7.6	11.3 ± 5.2
OS + W 200 °C	339.3 ± 20.6	186.2 ± 10.5
OS + W 300 °C	26.0 ± 7.6	26.4 ± 5.4
Cellulose	557.7 ± 50.5	340.9 ± 41.5

shows that the influence of oven temperature on the physical properties of the microwave-pretreated MSs is partly different from its influence on the microwave-treated MS + W.

Based on the elemental analysis of the pretreated straws, the content of carbon (C) and hydrogen (H) in the microwave-pretreated MS increased when the air temperature in the oven increased from 200 to 300 °C (Tables 1 and 2). Although pyrolysis was not performed in this study, the elemental composition changes in MS after microwave treatment were compared with the results of pyrolysis (or mild pyrolysis, which is torrefaction) as reported in the literature. Wang et al. (2009) reported that the carbon content of the straws gradually increases and the hydrogen content gradually decreases following microwave pyrolysis; my result is in good agreement with their findings (Table 2). A comparison of the elemental composition of chars from wet and dry pyrolysis demonstrates that chars from the dry pyrolysis of traditional feedstocks usually have higher carbon and lower hydrogen contents than those from wet pyrolysis (Libra et al., 2011). However, no significant correlation was observed between the elemental composition and the water content of the MS.

The C/N ratio in the pretreated MS was investigated because the C/N ratio of anaerobic feedstocks is significant for anaerobic digestion performance (Estevez et al., 2012). The C/N ratio analysis showed that when the temperature of the process was increased, the percentages of C and N in the pretreated MS decreased (Table 2). Although the C/N ratio in the pretreated MS was lower than that of the MS, it was still higher than the optimum C/N ratio of feedstock materials (between 20 and 30) (Estevez et al., 2012). Therefore, the pretreated MS still represents a good co-digestion biomass because it will provide higher carbon content for digestion.

In the other assessment of pretreated lignocellulosic biomass, the physicochemical parameters were measured, and the results of untreated and pretreated straws were compared to understand their physicochemical changes. This comparison indicates that the pretreated samples have physicochemical properties that are different from those of the untreated biomass (Tables 1 and 2). For example, when the temperature in the microwave oven increased to 200 °C, the pH of the pretreated straws decreased, as reported by Menardo et al. (2012). However, when the temperature in the oven increased from 200 to 300 °C, the pH of the pretreated straws increased to an even greater extent than the untreated MS. Heating until 240 °C as first step leads to the formation of char and volatiles (Lanzetta and Di Blasi, 1998). In general, the presence of oxygen yielded a lower pH value in the filtrate, most likely due to the solubilization of the acidic hemicelluloses components by the de-esterification of the acetate groups in hemicellulose, but also due to the oxidation of some hemicellulose and lignin fragments to carboxylic acids (Ahring et al., 1996).

In the present study, the conductivity results were similar to the pH results, except for SW (Table 2). The conductivity elements, which include micro-nutrients (e.g., Ca) and macro-nutrients (e.g., Fe and Mn) as well as some small amounts of organic matter that are dissolved in water, contribute to changes in the TDS value. It was reported that thermal treatment solubilizes the waste-activated sludge (Bougrier et al., 2008). However, when the TDS values of the pretreated straws for each pretreatment condition (at 200 and 300 °C) and for the untreated straws were compared, there was no relationship between the TDS value of the pretreated MSs and the pretreatment conditions (Tables 1 and 2). Similarly, a study on waste-activated sludge by Bougrier et al. (2008) indicated that, for temperatures lower than 200 °C, chemical oxygen demand (COD) solubilization of sludge was found to increase linearly with treatment temperature; however, for temperatures above 200 °C, the solubilization results seemed to be more dispersed. Some organic and inorganic products are released from the biomass due to the high temperature (Chen and Kuo, 2011). Because of these losses, the relationship between the TDS value of the pretreated MS and the pretreatment conditions was not determined in the study. In addition, one of the properties of the torrefied biomass (final solid product) was reported as hydrophobicity in the literature (Medic et al., 2012). Because thermochemical-treated biomass has strong hydrophobic properties and aromatic interactions between components such as phenolic moieties (Ku and Mun, 2006), the biomass might be a good candidate for adsorbent material; however, its properties can be affected by the solubility of the solid matter in the biomass.

As mentioned above, the effect of particle size was controlled in this work to remove the influences particle size on the compositional analysis of MS. Increasing the air temperature in the oven from 200 to 300 °C caused a decrease in the concentration of cellulose and hemicellulose in the pretreated MSs (Table 1). Similar results have been reported in the literature (Chen and Kuo, 2011; Demirbas, 2004; Mohan et al., 2006). As such, 180 °C has been identified as a key turning point in the microwave degradation of cellulose. Above this temperature, the specific microwave effect becomes pronounced, and the rate of degradation of cellulose increases significantly (Ahring et al., 1996) because microwave irradiation can damage and disrupt the structure of biomass due to the sudden temperature rise and the internal pressure increase. For example, the torrefaction at 260 °C caused a certain amount of hemicelluloses pyrolysis, whereas cellulose and lignin were only barely affected at this temperature (Chen and Kuo, 2011). Due to biomass torrefaction at 290 °C, large amounts of hemicelluloses and cellulose were destroyed. On the other hand, during the breakdown of hemicelluloses, inhibitory products are produced, such as phenolic and heterocyclic compounds, furfural and hydroxymethylfurfural. These inhibitory or toxic products have an adverse effect on the microorganisms during the subsequent bioconversion processes (Odhner et al., 2012). Therefore, when a thermal pretreatment is applied to lignocellulosic material, these unwanted products should be considered.

3.3. Conversion yield of the pretreatment

Table 2 shows the descriptive information for each straw, including the straw name and the temperature in the microwave

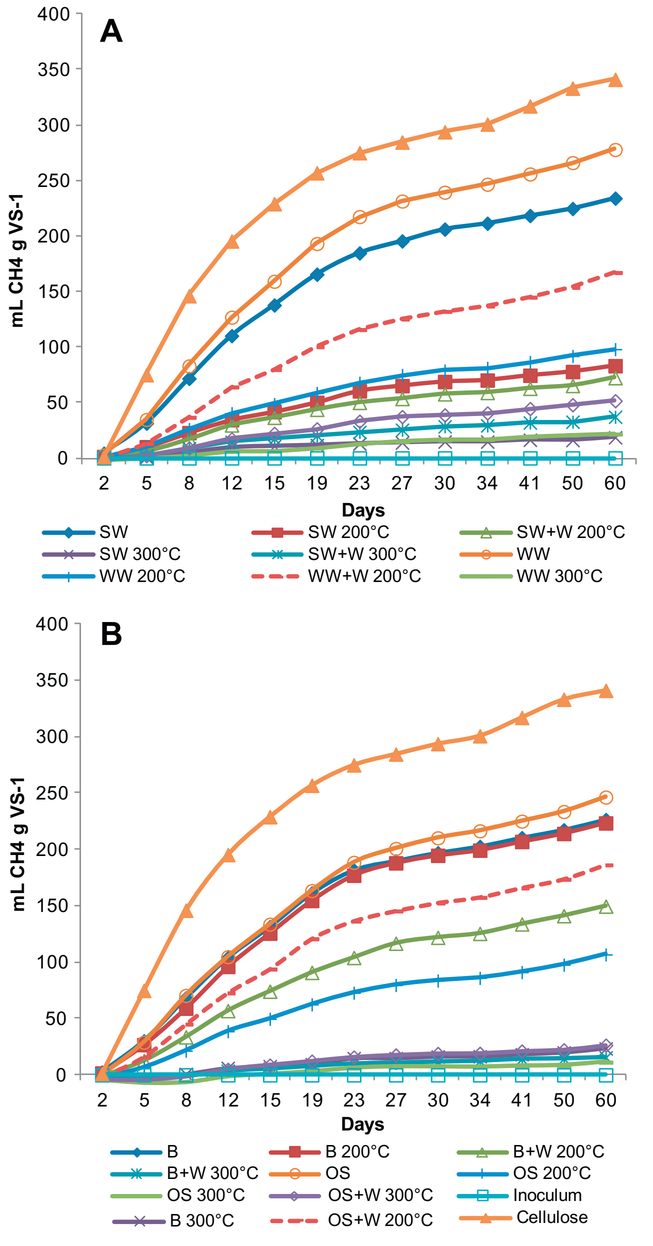

Fig. 2. Cumulative methane production yield from untreated and treated straws.

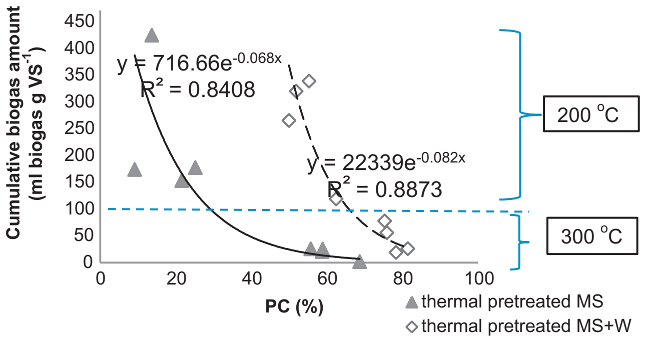

Fig. 3. Cumulative biogas amount as a function of the conversion yield (PC) of the microwave pretreatment process for dry straws (thermal pretreated MS) and wet straws (thermal pretreated MS + W).

oven and their experimental results, including the SY (%) and the PC (%). All the yields were calculated on a dry feed basis and were determined by the average of at least three experiments and the experimental errors were found to be lower than 11%. High experimental errors were observed due to the microwave-pretreatment of SW and B at 200 °C. Previously, it was mentioned that the thermocouple sensor was positioned inside of the microwave but not inside of the reactor. Wang et al. reported that char can absorb microwave energy, so the final temperature of char particles during microwave pyrolysis is likely higher than that of the surroundings (Wang et al., 2008).

As shown in Table 2, when the temperature was increased in the microwave oven, the SY decreased. The results also show that the SY is directly proportional to the moisture concentration of the straws (Table 2). A study on wheat straw using thermal gravimeter (TG) measurement, which provides information about temperature-dependent mass loss, showed a similar result to that of Stahl et al. (2004). Dry or wet pyrolysis has been used to carbonize biomass and to yield products with higher carbon contents. Compared with dry pyrolysis, wet pyrolysis produces higher solid yields, more water soluble organic compounds and fewer gases, especially CO_2 (Libra et al., 2011). Demirbas, 2004) obtained similar results in their study that examined the effect of the temperature and moisture content of feedstock on biochar yield. Moreover, in the present study, a high conversion ratio of the thermal pretreatment (PC) occurred at 300 °C instead of 200 °C (except for SW + W, which occurred at 200 °C in the trial) at 15 min holding period. The study by and Lanzetta and Di Blasi, 1998 showed that equilibrium moisture content and, presumably, extractives are released at low temperatures. Investigation of the torrefaction process based on the thermal degradation characteristics of five basic constituents (hemicellulose, cellulose, lignin, xylan and dextran were researched individually) and two pure materials (xylose and glucose) indicated that the torrefaction at 230 °C only released some moisture and light volatiles from the tested samples (Chen and Kuo, 2011). The changes in the volatile and fixed carbon contents were more pronounced between 400 and 500 °C in comparison to those higher temperatures, with the greatest volatile loss occurring below 500 °C (Zhu et al., 2010). Hence, the wet straws lost water molecules and some light volatiles until a temperature of 200 °C was reached. Upon further heating (from 200 to 300 °C), MS and MS + W lost the remaining light volatile fraction.

3.4. Effect of microwave pretreatment on biogas production

Biogas production from the untreated biomass (only milled) was found to be almost the same as the biogas production from cellulose ($p > 0.05$), which is easily digestible by bacteria (Table 3).

The external surface area of lignocellulosic materials is related to the size and shape of the particles, while the internal surface area depends on the capillary structure of cellulosic fibers (Taherzadeh and Karimi, 2008). Milling can be employed to alter the inherent ultrastructure of lignocelluloses and the degree of crystallinity and, consequently, can make it more amenable to degradation by cellulase. Therefore, reduction of the size of the straw samples mainly improved the digestibility of the straws by anaerobic bacteria, as previously reported by Menardo et al. (2012). The cumulative methane production from the WW (277.8 ml CH_4 gVS^{-1}) was similar to that reported by Jackowiak et al. (2011) (270 ml CH_4 gVS^{-1}), where 1-cm wheat straw cuttings were investigated for the same duration as in the present study.

As shown in Table 3 and Fig. 2, the untreated straws had significantly ($p < 0.05$) higher biogas and methane production than the microwave-pretreated straws (except B at 200 °C). In regards to the effect of the oven temperature on biogas production, the production of biogas of the pretreated straws at a low temperature (200 °C) was significantly higher ($p < 0.05$) than that of the pretreated straws at a higher temperature (300 °C). Similar results were also observed for methane production (Fig. 2). Jackowiak et al. (2011) have reported similar results for the yield of methane production from pretreated wheat straw based on microwave heating at 150 and 180 °C (maximum temperature used in their study). However, other studies of the microwave irradiation effect (range of 50–170 °C which was lower than the present study) on thickened waste-activated sewage sludge showed that sludge irradiated at 175 °C had the highest cumulative biogas production, which was approximately 31% higher than that of the control (Eskicioglu et al., 2009). When increased a pretreatment temperature from optimum temperature based on biogas yield, low biogas produced from the pretreated biomass was most likely due to microbial resistance, as reported by Medic et al. (2012). Therefore, depending on the feedstock type, the temperature in the oven should be considered for choosing the optimum pretreatment environmental conditions.

In other assessments for biogas production, the calculated PC yields from dry straws and wet straws were evaluated together with their biogas productions to understand the effect of microwave pretreatment. Fig. 3 shows that the cumulative amount of biogas from the pretreated MS and the pretreated MS + W decreased when PC yields increased. It was also observed that PC yields increased when the air temperature in the oven increased from 200 to 300 °C (Table 2). As previously mentioned, increasing the air temperature in the oven from 200 to 300 °C caused both a decrease in the hemicellulose content of the pretreated straws and, in contrast, an increase in the lignin content of the straws (Table 1). Thermal treatment $\geqslant$160 °C causes solubilization not only of hemicelluloses but also of lignin (Hendriks and Zeeman, 2009). Therefore, the increase in both the content and solubility of lignin was most likely due to the >160 °C process temperature in the present study. However, it has been reported that the compounds produced from the solubilization of lignin are very reactive and in many cases have an inhibitory or toxic effect on bacteria, yeast and methanogens/archaea due to the inhibition of biodegradation enzymes such as cellulase, xylanase, and glucosidase (Jackowiak et al., 2011; Taherzadeh and Karimi, 2008). The reason for the observed decrease in biogas productivity could be that products detrimental to anaerobic bacteria were produced during the microwave process.

The calculated PC yields from the pretreated MS were compared with the yields from the pretreated MS + W at the same temperature, based on their biogas production, to observe the effect of wet biomass. As observed in Fig. 3, the PC yields of the pretreated MS + W were calculated to be higher than the yields from the pretreated MS at the same temperature. As explained above, the higher PC yields of the pretreated MS + W were attributed to the release of moisture and some light volatiles. The pretreated MS + W produced higher cumulative biogas amounts than other samples with the same calculated PC yield. The high biogas production from the pretreated MS + W was most likely due to lower lignin content than the pretreated wet samples (Table 2) and/or more water-soluble organic compounds (Libra et al., 2011).

4. Conclusion

First, the high conversion ratio of the thermal pretreatment occurred at 300 °C rather than at 200 °C. However, the subsequent performance of anaerobic digestion in B, SW, WW and OS did not improve by increasing either the temperature in the oven or the water content in the straws in the microwave pretreatment. Second, the inverse relationship between conversion yield and cumulative biogas production was observed for both dry and wet straws. Based on these results obtained, the application of milling can be recommended as a pretreatment process for investigating MS types in biogas plants.

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